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Determining seasonal natural effects over isotopic baselines for CO_2 storage monitoring

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Abstract

Dissolved carbon stable isotopes in surface waters can be utilized as a monitoring tool of CO_2 geological storage and as a good indicator of potential CO_2 leakages, since each source of carbon has a specific isotopic signature. The isotopic carbon baseline value and its range will determine whether the situation responds to a leak or a natural modification as part of the system's annual cycle and its seasonal effects. We measured water temperature, pH, dissolved inorganic carbon (DIC) concentration and other geochemical variables, during the different annual stages, in order to characterize the contribution of different sources of carbon to the natural isotopic evolution of DIC in the area of Hontomin. This area is the selected site for the Spanish research facility for CO_2 geological storage operated by CIUDEN. The average value for δ^{13}C-DIC at the study site is -10.7 ‰ (V-PDB), which is very different of the CO_2 generated during the oxycombustion process (about -28 ‰ *vs* V-PDB). After statistical analysis of the sampling efforts, we observed light differences on their average isotopic values which imply certain seasonal effects, although we could not find effects over the DIC concentration.

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Keywords: CO_2 storage; stable isotopes; ^{13}C; monitoring; leak detection.

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1. Introduction

The concentration of atmospheric CO_2 has considerably increased from 280 ppmv to 380 ppmv over the last three centuries due to anthropogenic activities, including fossil fuel combustion. This increase in CO_2 and other greenhouse gases caused a rise in temperature that needs to be mitigated in order to prevent the irreversible environmental effects of climate change. To achieve this goal, the European Union's (EU) strategy for the reduction of CO_2 emissions includes the geological storage of CO_2 as one of the main options to try to reach energy sustainability and a 20% reduction in greenhouse gas emissions by 2020. The feasibility of this technology requires a multidisciplinary monitoring plan of the injected CO_2 as highlighted by the EU's directive (2009/31/EC) as it relates to geological storage of CO_2. Annex II of this directive requires the selection of techniques that can detect any leakage out of the storage complex to the subsurface or surface. However, isotope monitoring in surface water is still under development. In order to use this technique as a good leak detection indicator, it is important to state a baseline prior to injection to set the natural conditions of the ecosystem [1]. This isotopic baseline value and its range will contribute to the differentiation between a potential CO_2 leakage and a natural modification. The main advantage of this methodology is the quick identification of the DIC source and their possible alterations. By identifying the main source, small leakages from the storage formation can be discarded and changes will be attributed to natural modifications. We are aware of the importance of monitoring surface waters since CO_2 diffuse leakages can cause relevant alterations of ecosystems [2], agriculture damage and potential effects in the human health when reaching surface aquifers [3].

Since the geology remains stable with time, the processes that are conducive to variations in the DIC isotopic composition (δ^{13}C-DIC) are influenced by climate conditions and, especially temperature. The main sources of DIC in aquatic ecosystems correspond to dissolution of carbonates, community metabolism processes, and CO_2 exchange with the atmosphere. The dissolution of marine carbonate produces a little isotopic carbon fractionation in which the carbonate material presents a ^{13}C enrichment [4]. Hence, the remnant DIC in water reaches more negative δ^{13}C values in about 1 or 2 per mil. The community metabolism implies a biological process in the entire ecosystem. Photosynthetic blooms activate when attaining an optimal temperature, which depends on the geographical location and the involved species [5]. The major photosynthetic pathways, C3 route (tree, algae and aquatic plants and grass at middle and high latitudes) or C4 route (grass at lower latitudes), also cause different carbon fractionation [6]. During this process, the metabolic enzyme RuBisCo (C3 plants) discriminates against ^{13}C, rising the remnant DIC isotopic values towards more positive ones; if respiration processes are dominant, the isotopic pattern will be the opposite [7]. Lastly, the atmospheric exchange also plays a role in the DIC concentration and its isotopic composition. When the CO_2 diffuses into the water a fractionation process takes place due to the higher velocity of diffusion of ^{12}C versus ^{13}C, leading to a more negative value of DIC isotopic composition. In the case of degasification to the atmosphere, this trend turns into positive [8]. This CO_2 exchange depends on the temperature and partial pressure of CO_2 (pCO_2) compared to that of the atmosphere. A rise in temperature implies a decrease in the solubility of CO_2 in water, and the differences in pCO_2 will lead to the exchange of CO_2 in order to achieve the chemical equilibrium. The exchange is usually greater in the headstreams of rivers and in water bodies with low flux rates [9].

Every natural process described above and their seasonal variations over the isotopic values must be included in the baseline range in order to detect any possible modification to the system due to the anthropogenic activities. Therefore, the main objective of our study was setting the isotopic carbon baseline (δ^{13}C-DIC) for DIC in different surface waters across the North of Spain (Hontomin area) where CIUDEN storage project is being located. This CO_2 geological storage project is funded by the Spanish Government and co-financed by the EU through the European Energy Programme for Recovery.

2. Site of study

The study area covers an extent of 100 km square around the Hontomin village, in the north-central portion of the Iberian Peninsula, Spain (Fig. 1). This area has been extensively studied for oil exploration purposes. The CO_2 injection will take place within Lower Jurassic carbonates, at approximately 1500 meters depth. Upper Cretaceous marine carbonates and Cenozoic continental sediments (clay minerals and lacustrine carbonates) outcrop in the study area [10].

The sampling area is located in the confluence of two major river basins: the Duero Basin in the west and the Ebro Basin in the east. The water samples were taken from diverse rivers and springs around the injection area (Fig. 1), over a period of 30 months at all seasons. Following Köppen climate classification [11], the regional climate is type C, corresponding to template climates with a minimum average temperature between 0ºC and 18°C. This climate is divided in type Csb which corresponds with dry mild summers and Cfb which has no dry season and mild summer, both present in this region.

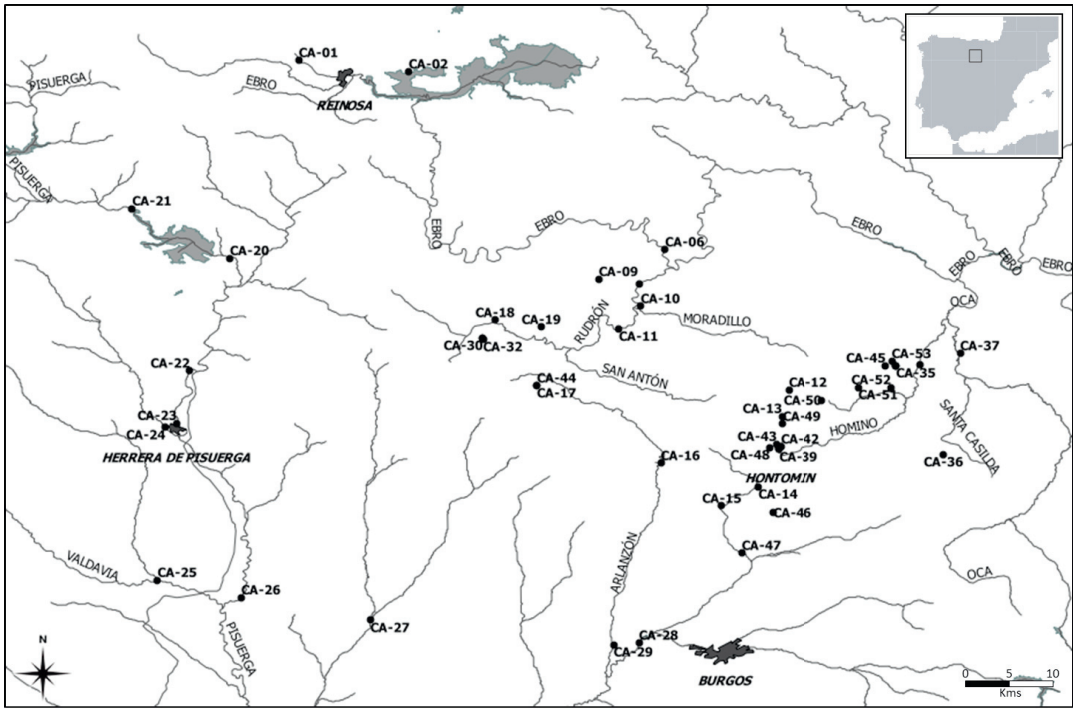

Fig. 1. Area of study and location of the sampling points. The triangle marks the injection area.

3. Methods

This study is based on six different sampling events spanning from February 2010 to May 2012. The purpose of these surveys was to cover the different climatic seasons and define the seasonal effects over the DIC isotopic composition in the study area. During the water sampling for isotopes, pH and water temperature data was collected in-situ. Climatic condition data covering the 30 months of study were obtained from the Spanish meteorological service (http://www.aemet.es).

In order to measure δ^{13}C-DIC values, each sample was filtered through a 0.45 μm cellulose acetate filter and preserved, immediately after collection, with mercuric chloride ($HgCl_2$) to avoid isotopic fractionation related to

biological activity. Three aliquots (0.5 mL) of each sample were reacted with 100% pure phosphoric acid in a closed system filled with 99.99% pure helium. The sample was reacted with phosphoric acid for 48 hours at 25°C constant temperature. During this period, the subsequent reactions transformed all DIC species to gaseous CO_2. This gaseous CO_2 was then easily removed from the aliquot by gas exchange in the headspace of the system. The isotopic composition was then measured in a Finnigan Delta Plus XP isotope ratio mass spectrometer attached to a Finnigan GasBench II, using CO_2 (99,995%) as a reference gas. The results are reported as $\delta^{13}C$ value relative to V-PDB standard, which is a Cretaceous belemnite from the PeeDee formation of South Carolina, United States [12]. The analytical precision is ±0.05‰, and the measurements are reproducible to ±0.1‰. The DIC concentrations were obtained simultaneously with the isotopic values through linear regression of the DIC internal standards used in this study. The concentration of each sample is proportional to the chromatographic area obtained during the isotopic measurements.

The pCO_2 in each sample was calculated using the program CO2SYS developed by Lewis and Wallace [13] with the temperature, pH values and DIC concentrations as input and assuming zero salinity. The Ca^{2+} concentration for each water sample were measured with a Varian ICP-720-ES, based on inductively coupled plasma-atomic emission spectrometry principles.

4. Results and discussion

Figure 2 presents the isotopic $\delta^{13}C$ signature in the area of Hontomin (modified from [14, 15]). In the upper part of the figure, the different superficial sources of carbon are represented. Only C3 plants have been considered due to the climatic conditions of the area. Soil CO_2 is about 4.5‰ heavier than its corresponding plant biomass (C3–C4) [16]. The isotopic difference between CO_2 and DIC depends on pH and temperature. This difference is around 0 ‰ at pH values close to 5, while it is relatively independent for pH values between 7.5 and 8 [17], becoming enriched by approximately 10 ‰. Therefore, and considering the relatively alkaline environment of the system, the effect of pH can be neglected, only considering the temperature effect. For the theoretical DIC isotopic calculation, we have considered temperatures of 0°C, 15°C and 30°C. Inorganic C sources, as well as the $\delta^{13}C$ values of dolomites and limestone from the system basement are plotted at the bottom of Figure 2.

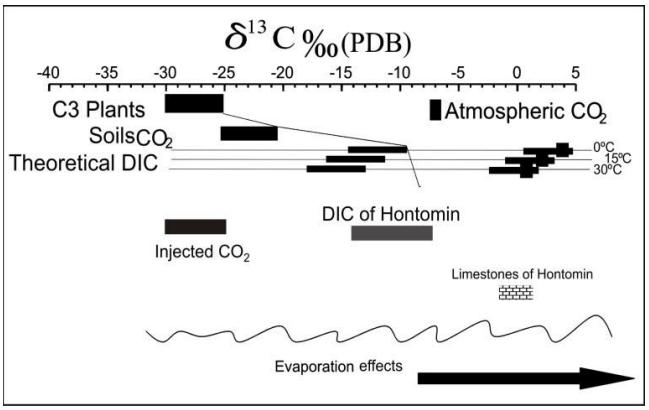

Fig. 2. The isotopic $\delta^{13}C$ signature of Hontomin area (Modified from [14, 15]).

After measuring the samples from the Hontomin area, we considered the values for the isotopic composition of dissolved inorganic carbon ($\delta^{13}C$-DIC) as the main indicator of changes in the surface aquatic systems. Figure 3 shows spatial and temporal variations in the $\delta^{13}C$-DIC values and concentration of DIC (Fig. 3) for each sampling site (Kruskal-Wallis, p-value < 0.001). A longer period of sampling is required in those locations showing wider ranges of isotopic values and concentrations in order to determine the seasonal component and to define their inclusion in the isotopic carbon baseline value calculated for the area. The $\delta^{13}C$-DIC values show a more stable

behavior than the DIC concentration. Thus, it will be easier to detect any anomalous variation due to anthropogenic carbon contributions.

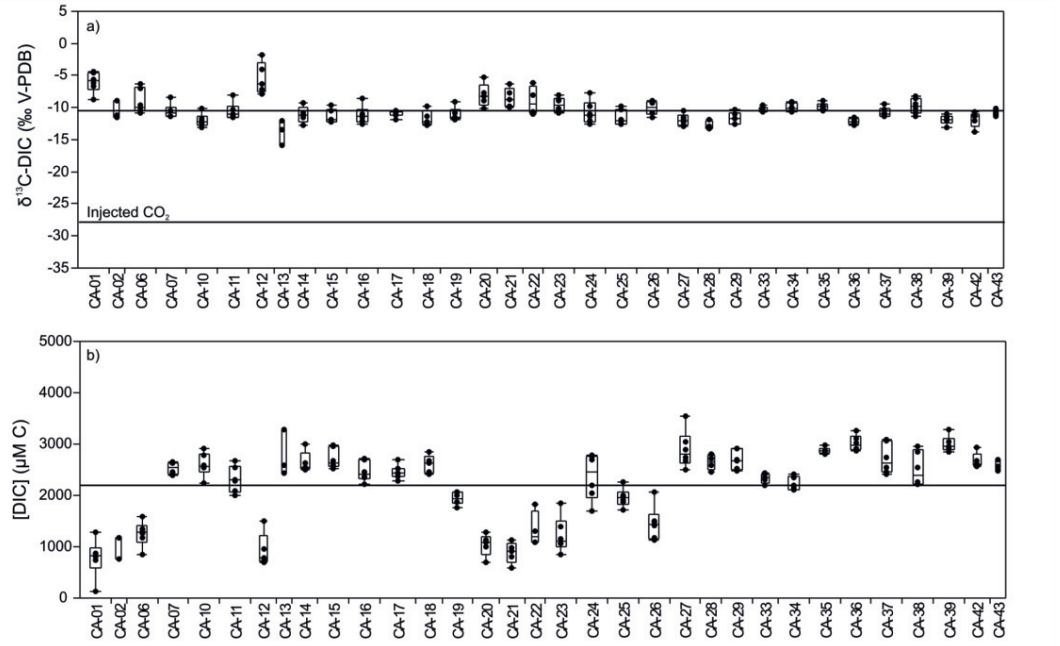

Fig. 3. (a) Isotopic composition of DIC (δ^{13}C-DIC), and (b) the concentration of DIC (μM C) measured at every point of study.

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The average isotopic values and other chemical and environmental variables for each sampling period are shown in table 1. In order to determine the seasonal effect, we compared the results obtained from each sampling effort. The global average value of the carbon isotopic composition in DIC is -10.7 ‰ V-PDB (Table 1) with a confidence interval ranging from -10.4 to -11.0 ‰ V-PDB. The analysis of the data reveals statistical differences in the δ^{13}C-DIC average values (Kruskal-Wallis, $p<0.0001$), implying certain seasonal effect (Fig. 4). The average concentration of dissolved inorganic carbon (2.2 mM C, Fig. 4) is on the same range of the global concentration for the major rivers in the planet, i.e. 0.9 mM C [18]. In order to evaluate the coherency of our results, we compared them to those obtained in the Rhône River (1-3 mM C and a δ^{13}C-DIC value of -5 to -10‰ V-PDB, [19]) and the Northeast US Rivers (0.6 mM C and a δ^{13}C-DIC value of -10‰ V-PDB, [20]). Although DIC isotopic values are very similar to those examples, the concentration is slightly different between studies since it depends on the amount of carbon released by the nearby source.

Table 1. Average values measured in the area of study.

Date	Air T (°C)	Water T (°C)	Rainfall (mm m^{-2})	pH	pCO_2 (ppmv)	δ^{13}C-DIC (‰V-PDB)	DIC (μM)	Ca^{2+} (μM)
Feb-2010	2.5	6.6	76.6	7.8	1796	-11.2	2363	1935
Jun-2010	13.1	14.4	63.9	--	--	-11.2	2322	1958
Jan-2011	2.9	8.6	87.3	7.8	1701	-11.8	2329	2099
Sep-2011	18.0	16.7	5.6	7.9	1554	-10.5	2146	1216
Feb-2012	1.7	9.1	37.6	7.9	1600	-10.2	2264	1443
May-2012	6.8	11.6	117.7	7.7	1879	-9.4	2114	1629
Average	7.5	11.2	64.8	7.8	1707	-10.7	2254	1707

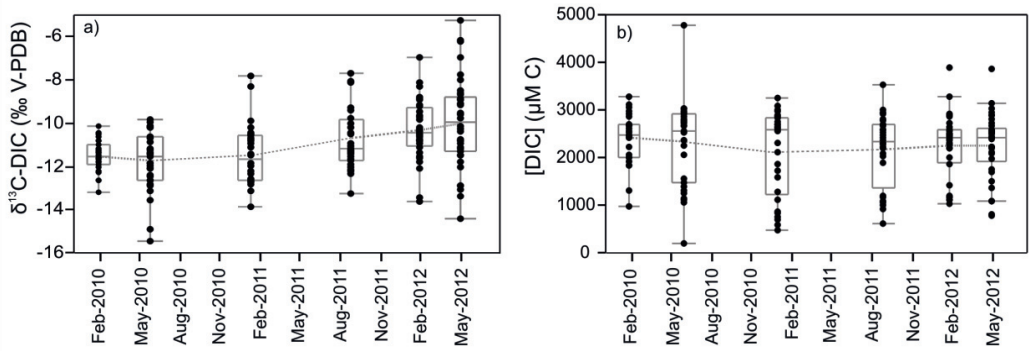

Fig. 4. (a) Temporal evolution of δ13C-DIC values and (b) concentration of DIC.

A general trend towards less negative δ^{13}C-DIC values during the warmer seasons, and more negative values during the colder periods was observed over the first four sampling events (Fig. 4). The first measured δ^{13}C-DIC value, in February 2010, was -11.2‰ V-PDB, while the last one, in May 2012, was -9.4‰ V-PDB. However, this apparent less negative trend could be biased by the time gaps between sampling events and the occurrence of an extreme climate event in this period. This event consisted on a large drought and high temperature period during 2011, leading to high water evaporation and vegetative stress that could have produced less negative δ^{13}C values as expected from respiration. Additionally, the enhancement of photosynthesis in aquatic systems preferentially removes ^{12}C. Consequently, the residual DIC will be enriched in ^{13}C (Table 1). This drought could have originated less negative isotopic values for the following months due to the dominance of the biological processes and a gradual increase of the partial pressure of CO_2 in water [21] as shown in Figure 6. The concentration of DIC was measured simultaneously with the δ^{13}C-DIC values and no statistical differences were observed between the mean concentrations identified in each sampling event (Kruskal-Wallis, p-values=0.7535). In fact, we noticed that the concentration of DIC appears to be constant through the entire study and without important seasonal effects (Fig. 4).

Finally, we organized the samples into two categories: samples collected during the cold season and samples collected during the warm season. We detected a little difference in the δ^{13}C-DIC average values ($\delta^{13}C\text{-}DIC_c$=-10.9‰ V-PDB, $\delta^{13}C\text{-}DIC_w$=-10.2‰ V-PDB, Kruskal-Wallis p-value=0.0256) and a higher variation on warm season values (Fig 5). However, we could not observe statistical difference for the DIC concentration (Kruskal-Wallis p-value=0.2446). Therefore, we carried out a more straight comparison of isotopic composition and concentration to study the temperature dependence. No clear statistical relation was found, although temperature plays an important role on those values [22]. This result indicates that the regional seasonal effects are masked by more than one process occurring simultaneously and also governed by the temperature.

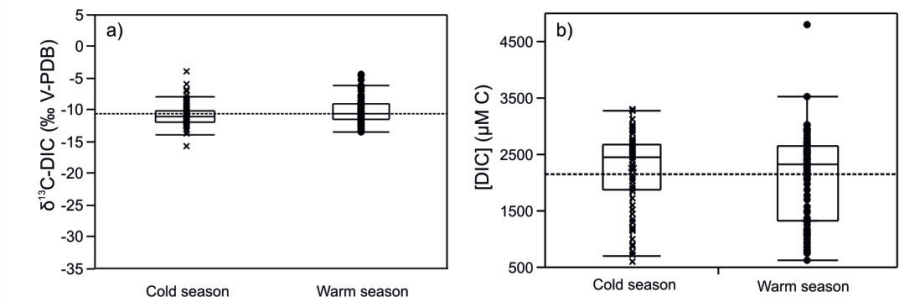

Fig. 5. (a) δ^{13}C-DIC values and (b) concentration of DIC during cold and warm season.

The pH in water regulates the distribution of chemical species in the carbon cycle, being HCO_3^- the most dominant when the pH ranges between 7.5 and 9.5 [23]. We observed that pH values present a constricted range of values between 7.7 and 7.9. Although subtle, there are perceptible statistical differences in the mean values, which suggest the presence of seasonal effects over the pH in the samples (Kruskal-Wallis, p-values=0.0128). When approaching the lower pH values, the concentration of DIC and Ca^{2+} (Fig. 6) in water rises, and the δ^{13}C-DIC decreases.

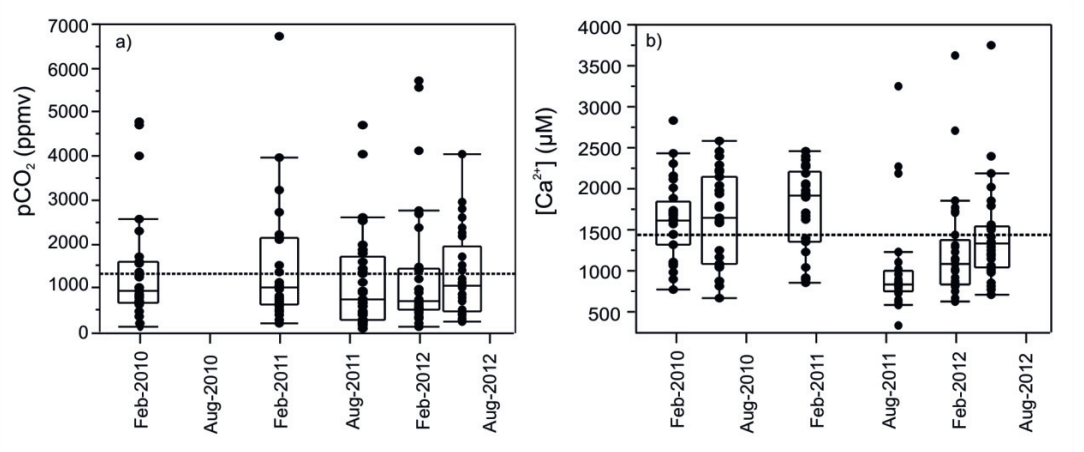

Fig. 6. (a) Temporal evolution of pCO_2 and (b) concentration of Ca^{2+} (µM).

The average value for the calculated partial pCO_2 is 1707 ppmv. No sensible statistical differences in pCO_2 average values were observed when comparing the different sampling events (Kruskal-Wallis, p-value=0.0933). This result implies that the pCO_2 is not affected by a seasonal effect. Nevertheless, a temporal pattern with higher values during winter and low values when the temperature rises is still noticeable (Fig. 6). The pCO_2 is similar to that observed in other studies for continental waters [24], and it suggests a general CO_2 degasification towards the atmosphere. The highest values occur during cold periods due to the increase of the solubility of CO_2 and, they drop considerably during warmer seasons, when the solubility in water is low and the enhanced photosynthetic processes during spring and summer takes place [21]. We found a change towards more positive values that can be caused by diverse biological and physicochemical effects and they generally have a seasonal pattern regulated by climate conditions and more specifically by the temperature.

5. Conclusions

δ^{13}C values (-10.7 ‰ V-PDB) and the DIC concentration were calculated in order to generate an isotopic baseline prior to the injection of CO_2 in the CO_2 geological storage site of Hontomín (Spain). In the study area, the main carbon source is vegetative decomposition and, in a lesser extent, the dissolution of carbonate materials and atmospheric CO_2. The different mechanisms acting simultaneously over the DIC isotopic composition have been identified as being the dissolution of carbonates, the community metabolism processes (respiration and photosynthesis), and the CO_2 degasification towards the atmosphere. Their dominance is dependent on the season in which the measurements are obtained, obtaining a more negative DIC isotopic composition in the cold season and less negative in the warm season. On the other hand, it is hard to define precise seasonal effects over DIC concentration due to the high variability of the samples. Finally, it is necessary to include extreme climate events such as droughts in the isotopic baseline to prevent errors during the detection of CO_2 leakages. Therefore, although the difference between the natural δ^{13}C values of DIC and the injected CO_2 is very important (about 18 ‰), it is of extreme importance to outline a natural carbon isotopic baseline prior to injection as a mechanism to control and detect leakages and prevent CO_2 reaching the surface waters.

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